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FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

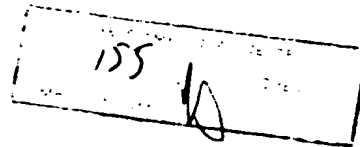
APPLICATION FOR A STANDARD PATENT

We, NALCO CHEMICAL COMPANY, incorporated in the State of Delaware, United States of America, of One Nalco Center, Naperville, Illinois, 60566, United States of America, hereby apply for the grant of a Standard Patent for an invention entitled:-

"OLEIC ACID AS A COEMULSIFIER IN WATER-IN-OIL LATEX POLYMERIZATION" which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 010,525
Country: United States of America
Date: 3rd February 1987



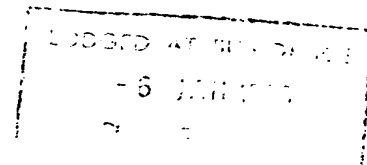
Our address for service is:

SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 5th day of January, 1988
NALCO CHEMICAL COMPANY

by 

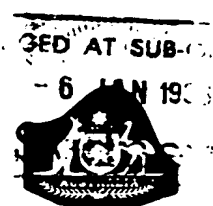
Law Institute of Patent Attorneys of Australia
of SHELSTON WATERS



To: The Commissioner of Patents
WODEN A.C.T. 2606

File: 135C

Fee: \$155.00



CONVENTION APPLICATION BY A COMPANY

FORM 8 - REGULATION 12 (2)

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

(a) Here insert (in full)
Name of Company.

In support of the Convention Application made by

(a) NALCO CHEMICAL COMPANY

(b) Here insert Title of
Invention.

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) "OLEIC ACID AS A COEMULSIFIER IN WATER-IN-OIL
LATEX POLYMERIZATION"

(c) and (d) Here insert
Full Name and Address
of Company Official
authorised to make
declaration.

(c) Milford B. Harp

of (d) One Nalco Center, Naperville, Illinois, 60566, U.S.A.

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was / were made

in (e) U.S.A. on the 3rd day of February, 1987

by (f) RADHAKRISHNAN SELVARJAN

in on the day of 19

by

in on the day of 19

by

in on the day of 19

by

(g) Here insert (in full)
Name and Address of
actual Inventor or
inventors.

3. (g) RADHAKRISHNAN SELVARJAN

of, 1177 S. Scoville, Oak Park, Illinois 60304, U.S.A.

is/are

the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the
Application are as follows:

Applicant is the Assignee of the said inventor.

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first
Application(s) made in a Convention country in respect of the invention, the subject of the
Application.

DECLARED at Naperville, Illinois

this 23 day of November 1987

(h) Personal Signature
of Declarant (c) (no seal,
witness or legalisation).

(h) *Milford B. Harp*
(Signature of Declarant)

(12) PATENT ABSTRACT (11) Document No. AU-A-10105/88
(19) AUSTRALIAN PATENT OFFICE

(54) Title

OLEIC ACID AS A COEMULSIFIER IN WATER-IN-OIL LATEX
POLYMERIZATION

(51)4 International Patent Classification

C08F 002/32 C08F 120/06 C08F 220/06

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SHELSTON WATERS

(57) Claim

1. A method for minimizing gel formation during the inverse water-in-oil emulsion polymerization process used to produce acrylic acid polymers which process uses a water-in-oil emulsifying agent which comprises using as a co-water-in-oil emulsifier from 0.5-2% by weight based on the weight of the emulsion of a C₁₂-C₂₂ fatty acid.

COMMONWEALTH OF AUSTRALIA

FORM 10

PATENTS ACT 1952

C O M P L E T E S P E C I F I C A T I O N

FOR OFFICE USE:

	Class	Int.Class
Application Number:		
Lodged:		

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name of Applicant: NALCO CHEMICAL COMPANY

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Actual Inventor: Radhakrishnan Selvarjan

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Complete Specification for the Invention entitled:

"OLEIC ACID AS A COEMULSIFIER IN WATER-IN-OIL LATEX POLYMERIZATION"

The following statement is a full description of this invention,
including the best method of performing it known to me/us:-

Introduction

A variety of water-soluble polymers may be prepared in the form of water-in-oil emulsions. See U.S. 3,284,393 which is incorporated herein by reference. When these emulsions are added to water in the presence of a water-soluble surfactant, they invert and allow the water-soluble polymers contained in the emulsion to rapidly dissolve in the water. These solubilization techniques are described in RE 28,474 and RE 28,576, the disclosures of which are incorporated herein by reference.

A common water-soluble polymer that is easy to synthesize in emulsion form and used in a variety of industrial applications in the form of dilute aqueous solutions thereof are the water-in-oil emulsions of acrylic acid polymers. Acrylic acid polymers, as this term is used herein, includes not only the water soluble forms of acrylic acid, e.g. the alkali metal, ammonia or amine salt forms thereof, but also includes copolymers of acrylic acid which contain as little as 50% by weight of acrylic acid. Typical of such polymers are acrylamide and sodium or ammonium acrylate copolymers.

20 Acrylic acid polymers in the emulsion form find application in the treatment of sodium aluminate solutions to remove the red mud impurities which solutions are formed by the practice of the Bayer process. For details of this technology, see Sibert, U.S. 3,390,959, the disclosure of which is incorporated here.

It has recently been observed that when these polymers are prepared using conventional water-in-oil emulsion polymerization techniques of the type disclosed in U.S. 3,284,393, small amounts of gel are formed. When the

water-in-oil emulsions of acrylic acid polymers containing such gel particles are inverted into water using pumps and similar devices, they cause clogging of circulation lines, screens, pump orifices, and the like. In certain instances the feeding devices tend to produce shear on the acrylic acid polymers causing additional gel formation. The present invention is specifically directed to minimizing gel formation which occurs during the water-in-oil polymerization of acrylic acid polymers.

The Invention

10 The invention comprises a method for minimizing gel formation during the inverse water-in-oil emulsion polymerization process used to produce acrylic acid polymers which process uses a water-in-oil emulsifying agent which comprises using as a co-water-in-oil emulsifier from 0.5-2% by weight based on the weight of the emulsion of a C₁₂-C₂₂ fatty acid.

 In a preferred embodiment of the invention the fatty acid is oleic acid.

THE WATER-IN-OIL EMULSIONS OF WATER-SOLUBLE ACRYLIC ACID POLYMERS

20 The water-in-oil emulsions of water-soluble acrylic acid polymers useful in this invention contain four basic components. These components and their weight percentages in the emulsions are listed below:

- A. Water-soluble acrylic acid polymer:
 - 1. Generally from 5-60%;
 - 2. Preferably from 20-50%; and
 - 3. Most preferably from 35-45%;

B. Water:

1. Generally from 20-90%;
2. Preferably from 20-70%; and
3. Most preferably from 30-55%;

C. Hydrophobic liquid:

1. Generally from 5-75%;
2. Preferably from 5-40%; and
3. Most preferably from 20-30%; and

D. Water-in-oil emulsifying agent:

1. Generally from 0.1-20%;
2. Preferably from 1-15%;
3. Most preferably from 1.2-10%.

It is also possible to further characterize the water-in-oil emulsions of water-soluble acrylic acid polymers with respect to the aqueous phase of the emulsions. This aqueous phase is generally defined as the sum of the polymer or copolymer present in the emulsion plus the amount of water present in the emulsion. This terminology may also be utilized in describing the water-in-oil emulsions which are useful in this invention. Utilizing this terminology, the aqueous phase of the water-in-oil emulsions of this invention generally consists of 25-95% by weight of the emulsion. Preferably, the aqueous phase is between 60-90% and most preferably from 65-85% by weight of the emulsion.

The emulsions also may be characterized in relation to the water/oil ratios. This figure is simply a ratio of the amount of water present in the emulsion divided by the amount of hydrophobic liquid present in the emulsion. Generally, the water-in-oil emulsions of this invention will have a water/oil ratio of from 0.25 to 18. Preferably, the water-in-oil ratio will range from 0.5-14, and most preferably from 1.0-2.75.

It is also contemplated as within the scope of the invention to use emulsions of the type described above which have been treated to remove substantially all the water therefrom.

The water-Soluble Acrylic Acid Polymers

As indicated, the acrylic acid polymers include not only acrylic acid and its water-soluble salts but also the copolymers with other water-soluble vinyl monomers such as acrylamide, methacrylamide, vinylpyrrolidone, itaconic acid, fumaric acid, and the like. In many cases, methacrylic acid polymers can be substituted as equivalents for the acrylic acid polymers.

When the polymers of the above type are used to remove the red mud impurities from aqueous solutions of sodium aluminate which are found in the manufacture of alumina by the Bayer process, it is customary to use acrylic acid homopolymers. Their molecular weights are preferably greater than 500,000 and are usually in excess of one million.

The Hydrophobic Liquids

The hydrophobic liquids or oils used in preparing these emulsions may be selected from a large group of organic liquids which include liquid hydrocarbons and substituted liquid hydrocarbons.

A preferred group of organic liquids that can be utilized in the practice of this invention are paraffinic hydrocarbon oils. Examples of these types of materials include a branch-chain isoparaffinic solvent sold by Humble Oil and Refinery Company under the tradename "Isopar M" described in

U.S. 3,624,019 and a paraffinic solvent sold by the Exxon Company, U.S.A. called "Low Odor Paraffinic Solvent". Typical specifications of this material are set forth below in Table I.

Table I

Specific Gravity 60°/60°F	0.780-0.806
Color, Saybolt	+ 30 min.
Appearance, visual	Bright and Clear
Aniline Point, °F, ASTM D-611	160 min.
Distillation, °F, ASTM D-86	
IBP	365 min.
FBP	505 max.
Flash Point, °F, TCC	140 min.
Sulfur, ppm, Microcoulometer	15 max.

While paraffinic oils are the preferred materials for use in preparing the water-in-oil emulsions of this invention, other organic liquids can be utilized. Thus, mineral oils, kerosenes, naphthas, and in certain instances petroleum may be used. While useful in this invention, solvents such as benzene, xylene, toluene, and other water immiscible hydrocarbons having low flash points or toxic properties are generally avoided due to problems associated with their handling.

The Water-In-Oil Emulsifying Agents

Any conventional water-in-oil emulsifying agent can be used such as sorbitan monostearate, sorbitan monooleate, and the so-called low HLB materials which are all documented in the literature and are summarized in the Atlas HLB Surfactants Selector. Although the mentioned emulsifiers are used in

producing good water-in-oil emulsions, other surfactants may be used as long as they are capable of producing these emulsions. It is also contemplated, however, that other water-in-oil emulsifying agents can be utilized.

U.S. Patent 3,997,492 shows the use of emulsifiers generally having higher HLB values to produce stable emulsions similar in character to those discussed above. With the use of the equations present in this reference, which is hereinafter incorporated by reference, emulsifiers having HLB values between 4-9 can be utilized in the practice of this invention.

In addition to the reference described above, U.S. 4,024,097 discloses particular emulsifying agents for the water-in-oil emulsions, which are the subject of this invention. These emulsions are generally prepared according to this reference utilizing a water-in-oil emulsifying agent comprising a partially esterified lower N,N-dialkanol substituted fatty amide. Additionally, other surfactants may be combined to produce emulsions having small particle sizes and excellent storage stability.

The Preparation of the Water-In-Oil Emulsions

Of Water-Soluble Acrylic Acid Polymers

The general method for the preparation of emulsions of the type described above is contained in Vanderhoff, U.S. 3,284,393. A typical procedure for preparing water-in-oil emulsions of this type includes preparing an aqueous solution of a water-soluble acrylic acid monomer and adding this solution to one of the hydrocarbon oils described above. With the addition

of a suitable water-in-oil emulsifying agent and under agitation, the emulsion is then subjected to free radical polymerization conditions and a water-in-oil emulsion of the water-soluble acrylic acid polymer is obtained. It should be pointed out that the ingredients are chosen based upon the weight percentages given above and their compatability with each other. As to choice of free radical catalyst, these materials may be either oil or water-soluble and may be from the group consisting of organic peroxides, Vazo type materials, redox type initiator systems, etc. Additionally, ultraviolet light, microwaves, etc. will also cause the polymerization of water-in-oil emulsions of this type.

In the manufacture of emulsions of this type, which are further detailed in U.S. 3,624,019, RE 28,474, U.S. 3,734,873, RE 28,576, U.S. 3,826,771, all of which are incorporated by reference. The use of air may be employed to control polymerization. This technique is described in U.S. 3,767,629 which is also hereinafter incorporated by reference.

In addition to the above references, U.S. 3,996,180 describes the preparation of water-in-oil emulsions of the types utilized in this invention by first forming an emulsion containing small particle size droplets between the oil, water, monomer and water-in-oil emulsifying agent utilizing a high shear mixing technique followed by subjecting this emulsion to free radical polymerization conditions. Also of interest is U.S. 4,024,097 which describes water-in-oil emulsions such as those described above utilizing particular surfactant systems for the water-in-oil emulsifying agent, allowing for the preparation of latexes having small polymer particle sizes and improved storage stability.

Another reference, U.S. 3,915,920, discloses stabilizing water-in-oil emulsions of the type above described utilizing various oil-soluble polymers such as polyisobutylene. Employment of techniques of this type provides for superior stabilized emulsions.

Of still further interest is U.S. 3,997,492 which describes the formation of water-in-oil emulsions of the type above described.

Physical Properties of
The Water-In-Oil Emulsions

The water-in-oil emulsions of the finely divided water-soluble acrylic acid polymers useful in this invention contain relatively large amounts of polymer. The polymers dispersed in the emulsion are quite stable when the particle size of the polymer is from the range of 0.1 microns up to about 5 microns. The preferred particle size is generally within the range of 0.2 microns to about 3 microns. A most preferred particle size is generally within the range of 0.2 to 2.0 microns.

The emulsions prepared having the above composition generally have a viscosity in the range of from 50 to 3,000 cps. It will be seen, however, that the viscosity of these emulsions can be affected greatly by increasing or decreasing the polymer content, oil content, or water content as well as the choice of a suitable water-in-oil emulsifier.

What is important in this invention is the fact that the emulsion be somewhat fluid, i.e. pumpable.

The Inversion of the Water-in-Oil Emulsions
of The Water-Soluble Acrylic Acid Polymers

10 The water-in-oil emulsions of the water-soluble acrylic acid polymers discussed above have unique ability to rapidly invert when added to aqueous solution in the presence of an inverting agent or physical stress. Upon inversion, the emulsion releases the polymer into water in a very short period of time when compared to the length of time required to dissolve a solid form of the polymer. This inversion technique is described in U.S. 3,624,019, hereinafter incorporated by reference. As stated in this reference, the polymer-containing emulsions may be inverted by any number of means. The most convenient means resides in the use of surfactant added to either the polymer-containing emulsion or the water into which it is to be placed. The placement of a surfactant into the water causes the emulsion to rapidly invert and release the polymer in the form of an aqueous solution. When this technique is used to invert the polymer-containing emulsions the amount of surfactant present in the water may vary over a range of 0.01 to 50% based on the
20 polymer. Good inversion often occurs within the range of 1.0-10% based on polymer.

The preferred surfactants utilized to cause the inversion of the water-in-oil emulsion of this invention when the emulsion is added to water are hydrophillic and are further characterized as being water soluble. Any hydrophillic type surfactant such as ethoxylated nonyl phenols, ethoxylated nonyl phenol formaldehyde resins, dioctyl esters of sodium succinate and octyl phenol polyethoxy ethanols, etc. can be used.

Preferred surfactants are generally nonyl phenols which have been ethoxylated with between 8-15 moles of ethylene oxide. A more complete list of surfactants used to invert the emulsion are found in Anderson, U.S. 3,624,019 at columns 4 and 5.

The Fatty Acids

10 The fatty acids used are those containing from 12-22 carbon atoms. The preferred fatty acids are the unsaturated acids containing at least 18 carbon atoms with a most preferred acid being oleic acid. It is understood that pure acids are not required to be used but so-called impure sources of fatty acids may be used such as the acids derived from vegetable oils and animal fats.

Thus, coconut oil fatty acids, palm oil fatty acids, corn oil fatty acids, tallow fatty acids, and the like may be used. Since the unsaturated acids give the best results as emulsion stabilizers, those acids derived from the vegetable oils are preferred.

20 The fatty acids are added to the starting ingredients prior to polymerization so as to provide between 0.5-2% by weight of the fatty acid based on the weight of the emulsion. A preferred range is .5-1.5% by weight.

The fatty acids in and of themselves, while capable of being used as the only emulsifier, it is preferred they be used in combination with the low HLB water-in-oil emulsifiers previously described.

Experimental

Ammonium acrylate monomer was obtained by neutralizing aqueous acrylic acid with ammonia. For the copolymer, mixed bed ion exchanged acrylamide solution containing 6-8 ppm copper was used. EDTA sodium salt and ammonium thiocyanate were used as the chelating agent and the polymer stabilizer, respectively. The monomer pH was 7.2 ± 0.1 and the polymerization was run in a batch mode at constant temperature. The azo initiators, Vazo 64/52¹, were used for polymerization. For oil phase, kerosene and LOPS from Exxon, and Drake OB-180 oil were evaluated. A water/oil phase ratio of 71/29 was maintained throughout.

The polymerization procedure is as follows: a water-in-oil emulsion was obtained by adding the monomer solution to the rapidly stirred oil phase containing the dissolved emulsifiers. Whenever a polymeric surfactant was used as a coemulsifier, homogenization of the water-in-oil mixture was carried out for 1-2 min. for optimum emulsification. The emulsion was stirred at 1,000 rpm for 15 min. with nitrogen purge. After the nitrogen prepurge, the emulsion temperature was raised to $42 \pm 1^\circ\text{C}$ and the initiator was dusted in. The polymerization was carried out isothermally and the conversion rate was determined by densitometry. A linear increase in density of the latex with conversion was observed due to a volume contraction. The conversion rate was determined from the slope of the conversion-time curve.

The RSV's¹, determined in 2M NaNO_3 for the homopolymer (at 0.04% conc') and in 1M NaNO_3 for the copolymer (0.45% conc'), were used as a measure of the polymer MW.

¹ Vazo 64/52 - 2,2'-Azobis isobutyronitrile/2,2'-Azobis (2,4-dimethyl) valeronitrile

² RSV - Reduced Specific Viscosity

For inversion test the following conditions were used:
1) at 70°F, 0.5% latex in 1% NaOH solution, and 2) at 130°F, 1% latex in 4% NaOH solution. The Brookfield viscosity at 15/20 min. gave the invertibility.

"Floc" test refers to the formation of a transient fluffy white "Floc" like material floating to the top of the inverted solution immediately after inversion. Upon continued mixing, the "Flocs" should disappear in 1.0-1.5 min. to pass the test. The "Floc" formation is due to the poor inversion of the latex.

The recirculation test equipment is composed of a reservoir (1 liter) fitted at the bottom with a 1/4" ID tube (recirculating loop) which passes through a gear pump. Recirculation test on a latex is carried out for 2 hours at a rate of 1 cycle/min., and the gel formed is determined gravimetrically.

Polyammonium acrylate latexes, converted into single components with fatty acids, met invertibility requirements and the recirculation test. These results are reported in Table I.

Table 1

Shear Stable Polyammonium Acrylate

Oil = LOPS, Polymer Solids = 40%, Polym'n pH = 7.3 ± 0.1,
 Polymer'n IOC/t hrs = 42-30/4, Post heat = 44-50°C/1 hr., Water-in-oil Phase Ratio = 71/29

Emulsifiers	Name/Name/Name	% BUL wt/wt/wt	Initiators		Polym'n Conversion Rate	HSV	Activators		Inversion @ 70°C Rate %	Floc Test	% Gel Recircul'n Test
			% BUL 64/52	% BUL 64/52			Name/Name	% BUL wt/wt			
	Span 80 ¹ /Tween 80 ² /-	1.68/0.32/-	0.06/-	0.06/-	-	24	Triton N-101 ⁴ / Brij 58 ⁵	1.54/0.46	93	Failed	-
	" /" /"	1.98/0.38/-	" /-	" /-	28	36.5	" /"	" /"	90	"	-
	" /" /"	2.47/0.47/-	" /-	" /-	35	34.0	" /Oleic acid	1.5/1.0	98	Passed	8.0
	" /Tween 61 ³ /-	1.25/0.75/-	" /-	" /-	-	26	" /Brij 58	1.5/0.5	91	Failed	-
	" /" /-	1.88/1.12/-	" /-	" /-	40	34.5	" /Oleic acid	0/0.4	85	Passed	0.3
	" /" /-	1.44/0.86/-	" /-	" /-	40	36.5	- /"	- /0.4	85	Passed	0.4
	" /" /Oleic acid	" /" /0.4	0.054/0.006	-	Microgel	-	-	-	-	-	-
	" /" /" /"	" /" /0.7	" /"	" /"	54	31.0	- /Oleic acid	- /1.1	91	Passed	0.2
	" /" /" /"	" /" /"	" /"	" /"	50	29.0	- /"	- /1.1	92	"	0.3
	" /" /" /"	" /" /"	" /"	" /"	"	32	- /"	- /1.1	"	"	0.5
	" /" /" /"	" /" /"	" /"	" /"	-	"	Triton N-101/ oleic acid	1.0/1.1	95	"	0.3

¹ Span 80 - Sorbitan monooleate

² Tween 80 - Polyethyleneoxy (20) sorbitan monooleate

³ Tween 61 - Polyethyleneoxy (4) sorbitan monostearate

⁴ Triton N-101 - Nonyl phenoxy polyethoxy ethanol

⁵ Brij 58 - Polyethyleneoxy (20) cetyl ether

* Acrylic acid aged for 8 months @ 25°C

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for minimizing gel formation during the inverse water-in-oil emulsion polymerization process used to produce acrylic acid polymers which process uses a water-in-oil emulsifying agent which comprises using as a co-water-in-oil emulsifier from 0.5-2% by weight based on the weight of the emulsion of a C₁₂-C₂₂ fatty acid.

2. The method of Claim 2 where the fatty acid is oleic acid.

DATED this 5th day of January, 1988

NALCO CHEMICAL COMPANY

Attorney: WILLIAM S. LLOYD
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS